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ORIGINAL ARTICLE

Electrochemical characterization of poly 3-thiopheneacetonitrile: Technique, solvent and relaxation effects

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Abstract Characterization and electosynthesis of 3-thiopheneacetonitrile (TA) on a platinum electrode have been studied. Different solvents such as Nitrobenzene (NB), 1,2-Dichloroethane (DCE), Dichloromethane (DCM) and Acetonitrile (AN) were used. Many techniques were used for the electrodeposition of films such as potentiodynamic, chronoamperometric and galvanostatic techniques. Poly 3-thiopheneacetonitrile PTA has been subjected to relaxation effect. When the polymer is left at a potential value in its insulating state for some time, the reverse peak in the voltammetric profile during the first positive run differs from the steady state wave. The effect of solvent on the relaxation of the polymer has been studied. A weak or no relaxation was found by using different solvents such as NB, DCE, and DCM.

1. Introduction

Since their discovery 20 years ago, a great attention has been paid to electronically conducting polymers because of the potential application in various fields, such as electrochromic and electroluminescent devices, electromagnetic interference shielding, sensors, etc. In the class of conducting polymers with a polythiophenes are particularly interesting due to their good stabilities in their doped and undoped states, and relative ease of functionalization (Skotheim et al., 1998). Polythiophene is the most attractive conducting polymer due to its superior characteristics and structural versatility. However, the electro-oxidative polymerization method has been preferentially used for the preparation of polythiophene films, because the deposition can be easily controlled by electrochemical techniques (De Oliveira et al., 2000; Malta et al., 2003).

In our previous work (Abou-Elenien et al., 2004; El-Maghraby et al., 2010) we had been found that the parameters such as applied potential, charge density, electrolytic media, solvents, used techniques, and the temperature have an effect on the relaxation process. The electrochemical synthesis was found to be difficult requiring a higher oxidation potential with respect to 3-alkyl substituted thiophene and leading to the obtainment of short oligomers (Waltman et al., 1983).

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The slow relaxation of conducting polymers (CPs) is an interesting phenomenon which has been extensively studied theoretically or experimentally by many researchers from different field of science (Nateghi and Zarandi, 2008). In cyclic voltammetry experiments, the oxidation peak of the first run after the sample has been left for a wait-time in the neutral state, is narrower and shifted toward more positive potential than the peak observed in steady state conditions (Odin and Nechtschein, 1991). This process is reported as the slow relaxation effect or memory effect by most of researchers. A complete description of this effect is yet to be developed and the mechanism is still under debate (Abou-Elenien et al., 2004; Aoki et al., 1998).

In the potentiodynamic 3-((*w*-Bromoalkyloxy)methyl)thiophenes polymerization, the oxidation potential shifts to more anodic values as the number of scan increases indicting that the resistivity of the film increases, i.e. is difficult to be oxidized. This was not so for the cathodic scan, this related to the side-chain would generate distortion of the polymer chain, breaking up their planarity, and the conjugation would be interrupted (Soto et al., 2008).

In chronoamperometric deposition, following the initial spike, the current falls to a minimum and then rises to a plateau (Albery et al., 1991). This feature together with the current cross-over in the potentiodynamic technique during polymer deposition under swept potential control (Li and Albery, 1992) is typical of deposition through a nucleation and growth mechanism (Asavapiriyanont et al., 1984; Fleischmann and Thirsk, 1963; De Levie, 1984; Rehback et al., 1987). The bidimensional contribution decreases as a result of solvent effect on polythiophene can be explained considering that the more polar solvent molecules are more strongly adsorbed on the electrode and prevent the adsorption of short chain oligomers. The solubility of the oligomers decreases as the polarity of the solvent increases (Del Valle et al., 2002). The electropolymerization of 3-thiopheneacetonitrile TA was initially performed in acetonitrile solvent (Roncali, 1992). The authors stated that, thin film of 3-thiopheneacetonitrile and 3-bromothiophene adhered onto Pt could be obtained. However, films are produced only when these monomers are oxidized at ca. 100 mV above their oxidation peak values. Simultaneously, the solution became colored near the Pt electrode surface, and much diffusion into the solvent was observed. This suggests that a significant amount of short-chain oligmers (dimmers) is being formed which is stable enough to diffuse away from the electrode. The bulky β-substituents may hinder chain propagation by steric crowding, thereby giving rise to a more nonplanar polymer.

Earlier studies (Waltman and Bargon, 1986) with poly 3-thiopheneacetonitrile PTA reported that the electropolymerization of TA, and of 3-bromo- and 3,4-dibromothiophene is accompanied by much discoloration of the acetonitrile solution. This suggests that significant amounts of soluble products are produced simultaneously with the film-forming reaction. Strongly electron-withdrawing groups destabilize the radical–cation intermediate such that its decreased lifetime favors rapid reaction with solvent or anions to form soluble products, rather than to electropolymerize (Waltman and Bargon, 1986). For polybithiophene, the two reduction peaks may be associated with expulsion of anion from two discrete parts of the polymer or the first response may be anion expulsion with the latter cation incorporation to balance negative charge in responses where anion expulsion is difficult (Cutler et al., 2002).

In galavanostatic method, the amount of polymer deposited on the electrode surface strongly depends on the current density applied. The amount of polymer deposited onto the electrode surface increases with the increasing current density although, when very high current density was applied, oligomeric species fell down from the polymer to the solution (Ocon et al., 2001).

In this paper, I report the results obtained in the electropolymerization processes of 3-thiopheneacetonitrile on Pt using different solvents media and tetrabutylammonium hexafluorophosphate as electrolyte. A group of parameters such as solvent effect, electrochemical techniques, relaxation effect have been studied. The correlation between the electropolymerization and the relaxation is discussed. My aim has been to study poly 3-thiopheneacetonitrile which is rarely mentioned in the literature. These results were compared with those obtained in previous work of polyalkylthiophenes.

2. Experimental

The experimental methodology and conditions are the same as reported in the previous study realized with 3-alkylthiophenes in different solvents (Abou-Elenien et al., 2004; El-Maghraby et al., 2010).

2.1. Starting material

3-Thiopheneacetonitrile (TA) was of reagent grade and used as received from commercial source (Sigma–Aldrich). Nitrobenzene (NB) [Aldrich], 1,2-Dichloroethane (DCE) [HPLC-pure grade (Fisons Scientific Equipment Incorporating Griffin & George England)], Dichloromethane (DCM) and Acetonitrile (AN) [HPLC-pure grade (Fisons Scientific Equipment Incorporating Griffin & George England)]. All the solvents (NB, DCE, AN & DCM) were used as received from commercial source. Before each measurement the solvents are allowed to pass over aluminum oxide (Super I ICN) under dry argon atmosphere (Abou-Elenien et al., 2001).

Tetrabuthylammoniom hexafluorophosphate $TBAPF_6$ (Aldrich) was used as the supporting electrolyte. The electrolyte was purified recrystallized grined, dried under vacuum for 5 h and stored under argon atmosphere (Luder and Krauss, 1963).

2.2. Elecrosynthesis

Platinum disc electrode was used for electropolymerization. Many techniques were used for the electrodeposition of films such as potentiostatic, potentiodynamic, chronoamperometric and galvanostatic techniques. The thickness of the doped conducting film was controlled by the electrolysis time. In potentiostatic and potentiodynamic electrosynthesis the scan rate (50 mV/s) started from the rest potential of the working electrode. The polymer films were grown by electrooxidation of the monomer by repetitive potential cycling between the cathodic and anodic potential limits. In chronoamperometric electrodeposition the working electrode was first switched from the rest potential to value prior to the redox potential for a period of 1 min. Polymerization was achieved by further step

to potentials close to peak potential of the monomer. In galvanostatic technique it selected the better current density value to obtain a very stable-film. After polymerization, the film was rinsed thoroughly with the same solvent used and transferred into a new degassed supporting electrolytic medium involving solvent and supporting electrolyte. Then, the film was electrochemically reduced at potential according to insulating state for 1 min. The stability in electrolytic medium has also been determined after 10 cycles between oxidized and reduced state.

2.3. Characterization and measurements

The EG&G Princeton Applied Research Model 283 Potentiostat/Galvanostat Controlled from a PS-486-DX microcomputer via a National Instrument IEEE-488 through GPIB board by means of M270/250 Program was used for the electrochemical control. However, all the potentials were cited with respect to Ag wire reference electrode. A platinum sheet (1×1)-cm^2 with a Teflon head was used as auxiliary electrode. The auxiliary electrode is dipped in 65% HNO_3 followed by washing several times with distilled water and dried in an electrical oven at 150 °C. The temperature in all studies was controlled by using cryostat of model RC20 CS Lauda. Discussion and potential sequence was displayed in details in previous work (Abou-Elenien et al., 2004).

3. Results and discussion

Fig. 1 shows the cyclic voltammogram of 3-thiopheneacetonitrile TA in dichloromethane with $TBAPF_6$ as supporting electrolyte with scan rate 50 mV s^{-1} at Pt electrode. In the anodic scan, the oxidation of TA start at potential of about 1.82 V. This could be due to the electronic withdrawing effect of the $-CH_2CN$ on the electron density of the thiophenic ring. An anodic shoulder at about 1.9 V together with a cathodic signal is evident in the oxidation process.

The electrochemical characterization of the monomer and polymer in different solvents is summarized in Table 1. Different solvents used such as nitrobenzene NB, Dichloroethane DCE, Dichloromethane DCM, and acetonitrile AN for electrosynthesis of poly 3-thiopheneacetonitrile PAT. These solvents have been chosen because of a difference in the donor number (DN) (Reimers and Hall, 1999). Different supporting electrolyte such as tetrabutyle ammonium hexafluorophosphate $TBAPF_6$, tetarabutyl ammonium perchlorate $TBAClO_4$, tetaraethyl ammonium perchlorate $TEAClO_4$, and lithium perchlorate $LiClO_4$ are used. As previously mentioned (Abou-Elenien et al., 2004) it was found that, the most stable film was obtained by using $TBAPF_6$.

The temperature of electropolymerization has been reported to affect the extent of the conjugation system and hence the optical and electrical properties of the polymer, the films produced at high temperature having a shorter mean conjugation length than those prepared at low temperature (Roncali, 1992). By controlling the temperature of the experiment during the film building, it was found that the most stable TA film was obtained at 5 °C.

In previous study (Abou-Elenien et al., 2004) it was observed that during scanning toward more positive potential the film was conducting and the response of the oxidation peak of the ferrocene appeared in both coated film and bar electrode while in reduction state, the film insulating and reduction peak of cobaltocene did not appear. The conductivity of the 3-thiopheneacetonitrile was checked and the response of the film using ferrocene and cobaltocene gave the same result as before (Abou-Elenien et al., 2004; Audebert and Bidan, 1985).

In this work, electrochemical polymerization of the monomer can be carried out by either potentiodynamic, chronoamperometric, or galvanostatic methods using a typical coating solution of 0.2 M monomers in the selected solvent. In potentiodynamic method the thickness of the film was controlled through the number of cycles. For other techniques the thickness of the film was controlled by electrolysis time until a given

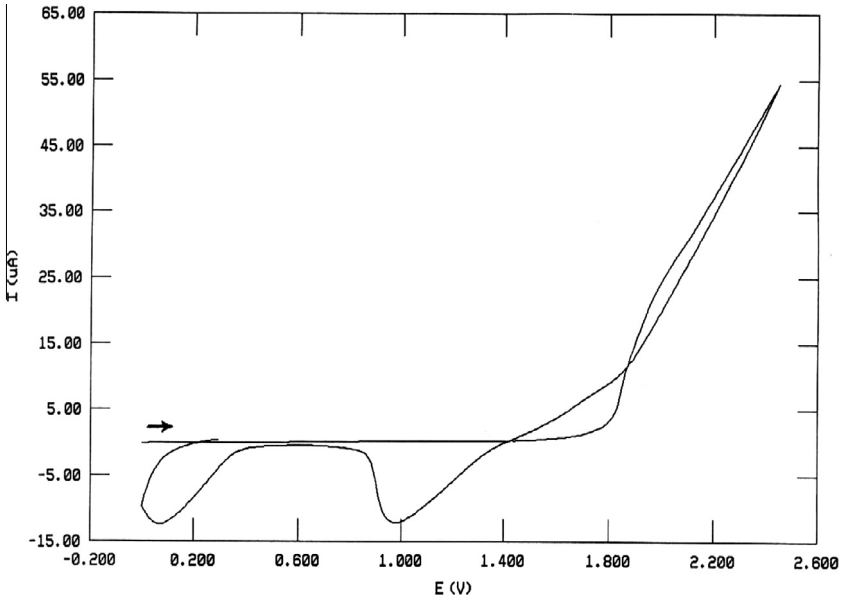

Figure 1 Cyclic voltammogram of 0.2 M 3-thiopheneacetonitrile in DCM and 0.02 M $TBAPF_6$ at Pt-electrode with scan rate = 50 mV s^{-1}.

Table 1 The electrochemical characterization of the investigated compound.

Compound[a]	Solvents[b]	DN	E_{ox} monomer (mV)	E_{ox} polymer (mV)
TA	AN	14.1	2190	1760
	NB	8.1	2320	1560
	DCM	4	2170	1520
	DCE	0.1	2289	1610

[a] Peak potential measured relative to Ag wire reference electrode.
[b] $TBAPF_6$ was used as supporting electrolyte.

amount of the total anodic charge had passed. The films obtained using AN solvent have low stability as compared with those obtained using other solvents. Fig. 2 shows the results for the polymerization of TA in different solvents. This profile shows successive cyclic voltammograms corresponding to the electropolymerization of TA at Pt-electrode from solution of 0.2 M monomer and 0.02 $TBAPF_6$ in (A) NB, (B) DCE, (C) DCM, and (D) AN, all at scan rate 50 mV s^{-1} and the film was stable. As shown from the curves, there is a shift in the oxidation peaks to the anodic potential. The shift of the oxidation peak to higher potential is due to the thickness of the film obtained by casting: the polymer became unswollen and no appreciable amount of electrolyte results present within it to allows fast oxidation (Soto et al. 2008; Ballarin et al., 2007; Zotti and Schiavon, 1989). By the same method stable film was obtained in DCE solvent. In the case of acetonitrile, the film had less stability at the same condition of concentration although the potential sweep appears cross-over. The film

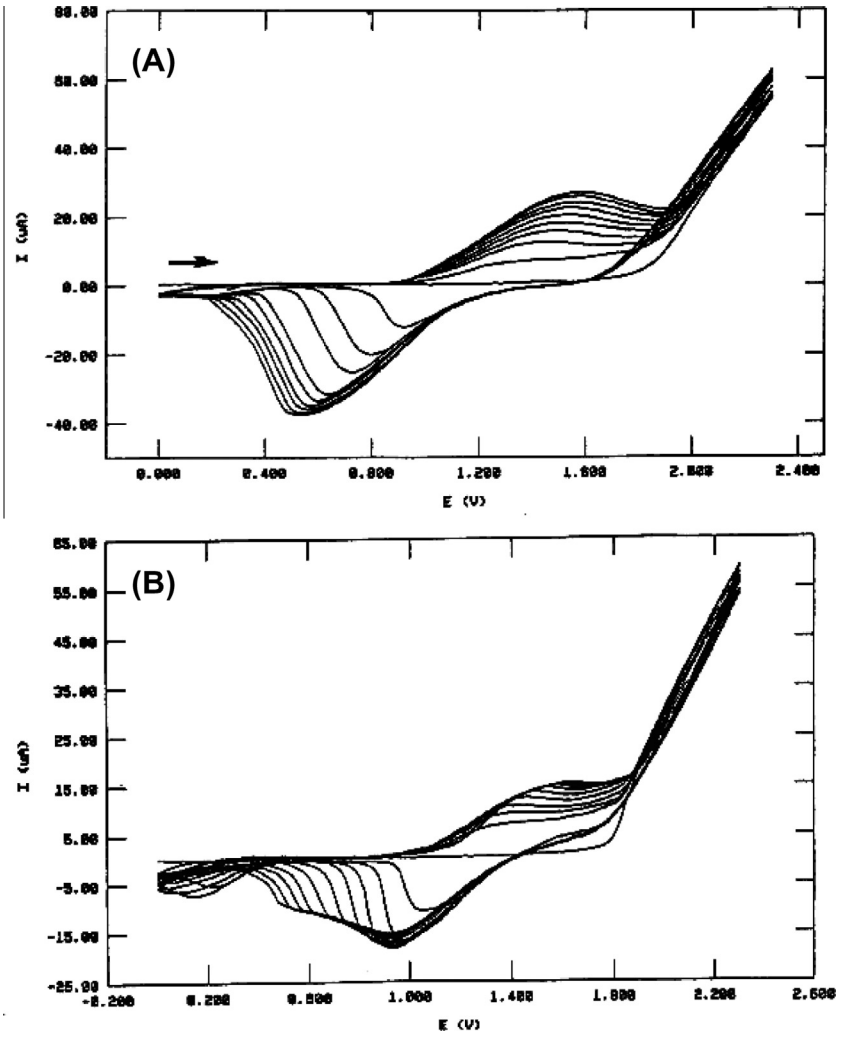

Figure 2 Successive cyclic voltammograms corresponding to the electropolymerization of 3-thiopheneacetonitrile at Pt-electrode from solution of 0.2 M monomer in: (A) NB, (B) DCE, (C) DCM and (D) 0.4 M monomer in AN; with 0.02 M $TBAPF_6$; at scan rate 50 mV s^{-1}.

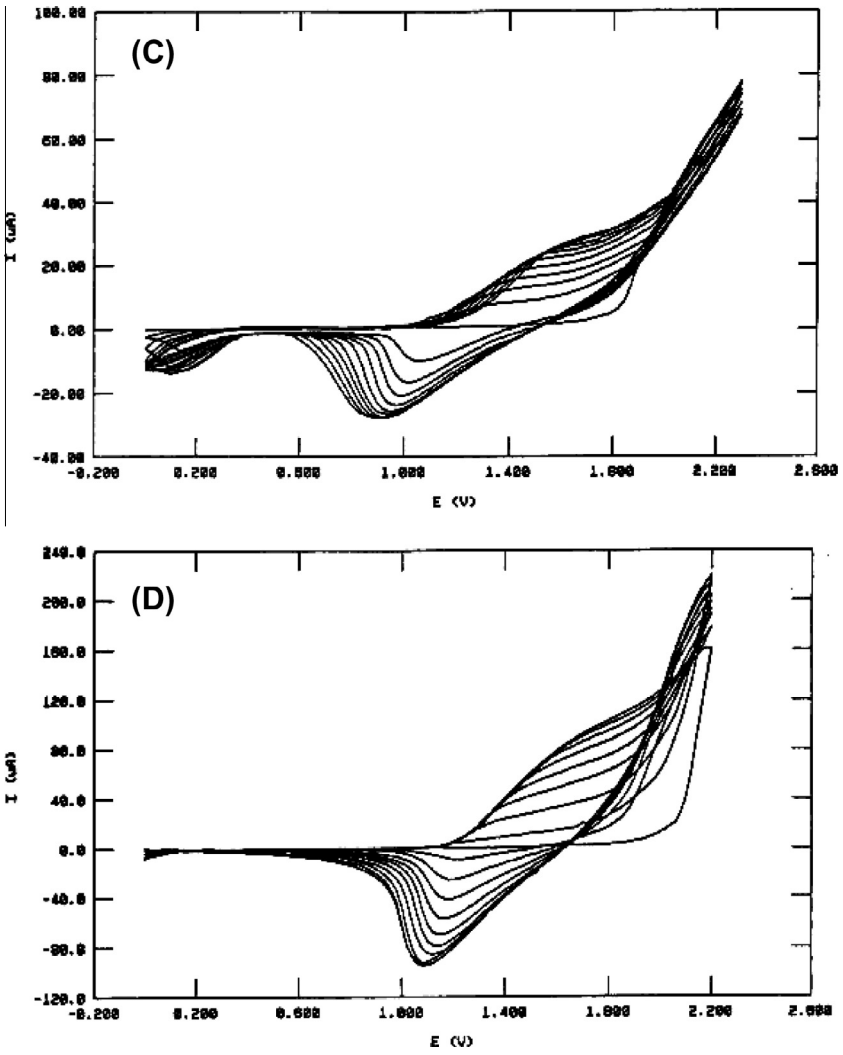

Fig 2. *(continued)*

obtained in AN was less stable through a wide range of monomer concentration. In the cyclic voltammetry curves for polymerization notably the first cycle, the anodic current is even bigger during the early reverse scan than during the forward scan, leading to across-over. However, the best film obtained using nitrobenzene solvent. This is in agreement with the literature (Roncali, 1992).

Chronoamperometric curves in Fig. 3 were recorded at the potential electrode of 2.3 V in 0.2 M DCE, DCM, NB and 0.4 M AN solvents with 0.02 M $TBAPF_6$, pointing out that the high applied potential produced high amount of polymer on the electrode surface (Ruiz et al., 2004). Upon compression, typical electropolymerization chronoamperogram was obtained in the case of DCM and DCE. So that very stable films obtained chronoamperometrically using DCE and DCM, as shown from Fig. 3. The minimum value of current is achieved when nucleation stage starts; this step goes on until the current becomes nearly constant, which means that the polymer growth takes place. In all cases, stable film were obtained in 0.2 M monomer except AN in which 0.4 M monomer needed to obtain relative stable film. It could be seen that, in the potential step the current quickly increased into a value more higher than that for other solvents. It is well known that anodic electropolymerization process takes place in two clear stages: nucleation and polymer growth. The whole process is highly influenced by the anodic potential applied to the working electrode, as has been previously reported (Ruiz et al., 2001; Du and Wang, 2003).

For a galvanostatic method, the almost constant potential through the whole process using galvanostatic condition indicated the formation of well conducting films (Visy et al., 1996, 1997). The electrosynthesized films display good adherence into the electrode surface. The electrode coating is homogeneous. The optimal current density for the galavanostatic generation is ca. 5 mA\cm^2. Fig. 4 shows synthesis in galvanostatic mode of 3-thiopheneacetonitrile on Pt electrode using 0.2 M monomer with 0.02 M $TBAPF_6$ supporting electrolyte solution in different solvents applied current density of 5 mA\cm^2. A facilitate PTA deposition could be achieved by inspection of the chronopotentiogram. The potential was stabilized in all investigated solvents near ca. 2.4 V (DCE, DCM, NB) and 2.1 V AN vs Ag reference electrode.

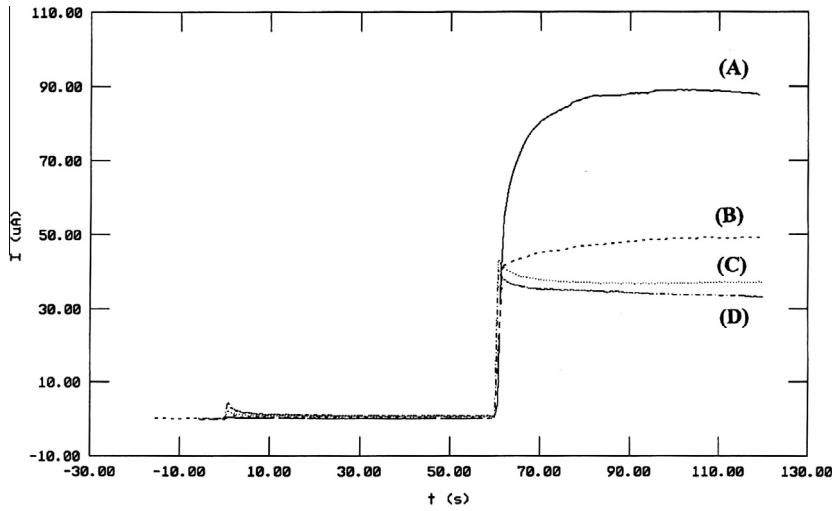

Figure 3 Chronoamperometric responses for the electropolymerization of 3-thiophene acetonitrile onto Pt-electrode from solution of 0.2 M monomer and 0.05 M $TBAPF_6$ in different solvents: (A) 0.4 M monomer for AN; (B) NB; (C) DCE; (D) DCM.

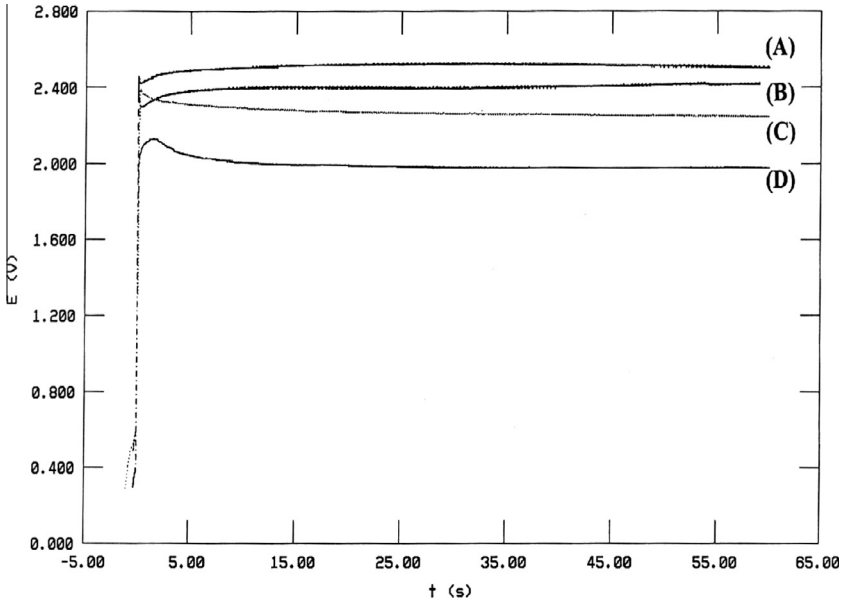

Figure 4 Typical chronopotentiogram obtained during galvanoststic polymerization of 3-thiopheneacetonitrile onto Pt-electrode at 5 mA/cm^2 current density from solution of 0.2 M monomer and 0.02 M $TBAPF_6$ in different solvents: (A) DCE; (B) DCM; (C) NB; (D) AN.

3.1. Relaxation measurement

Fig. 5 shows the cyclic voltammograms of PTA in different solvents: (A) film synthesized in NB and transferred into NB/0.02 M $TBAPF_6$ (B) film synthesized in DCM and transferred into DCM/0.02 M $TBAPF_6$ (C) film synthesized in DCE and transferred into DCE/0.02 M $TBAPF_6$. Good wave of PTA film was obtained in NB as compared with other solvents. The broadness of the mean wave is attributed to the breadth of the distribution of conjugated chain lengths of varying redox potentials and accessibility for electron exchange in the polymer lattice (Frank et al., 1989). Generally, the relaxation study was carried out by the same way as before in previous work (Abou-Elenien et al., 2004). After electropolymerization of the PTA film was rinsed with dry solvent to get rid of the monomer and then immersed in dry electrolyte solution in which the film was reduced into neutral state and subjected to 10 cycles between the oxidation and reduction potentials. This process participates in the stability of the film in solution (Rasch and Vielstich, 1994). The properties of the films are strongly influenced by the polymerization potential. High potentials, necessary for the polymerization of TA, cause an irreversible oxidation of the polymer chains.

The potential sequence used in the present relaxation studies was mentioned in detail previously (Abou-Elenien et al., 2004). The relaxation of the film is followed up recording

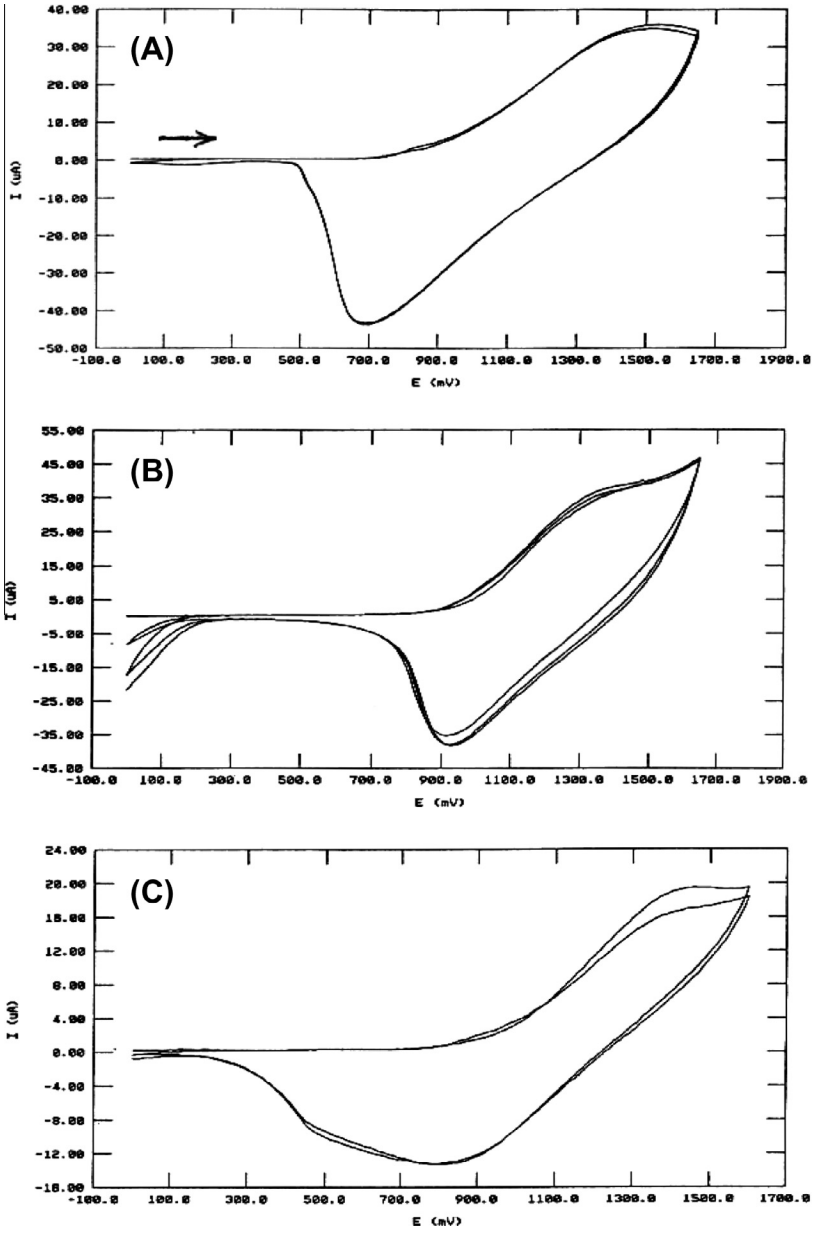

Figure 5 Cyclic voltammogram of PTA films on Pt-electrode; wait potential E_w = 0 V, scan rate = 100 mV/s; the films were galavanostatically electrosynthesised in: (A) NB and transferred into NB/0.02 M $TBAPF_6$ (B) DCM and transferred into DCM/0.02 M $TBAPF_6$ (C) DCE and transferred into DCE/0.02 M $TBAPF_6$.

two successive cyclic voltammograms after different wait time in open circuit condition. The relaxed peak (first run) is shifted to more positive potential and had a higher peak current than the steady state peak (second run). In the relaxation study (Otero et al., 1997; Otero and Grande, 1999) presented a model of electrochemically stimulated conformational relaxation (ESCR). In this model, the films of CP (polypyrrol) have a compacted and closed structure in their reduced state, and longer cathodic reduction times promote a higher compactness, hindering the exchange of counter anions between the solution and polymer film. This is in agreement with our work in which during oxidation of the polymer film at very low temperature with prepolarization the film became nonconducting and no peak appeared. This is in agreement with other work. Peter and co-workers developed a complex model, involving fast and slow ion ingress and egress, and acid–base equilibration processes for polyaniline (PANI), explaining the electroactivity of this conducting polymer and a slow relaxation SR phenomenon observed (Peter et al., 1991). Mažeikiene· and Malinauskas (2002) studied the slow relaxation with respect to the dependence of SR on polyaniline film thickness, waiting potential. They found a weak or no SR by extending the waiting potential over 0.05 V versus Ag/AgCl. They concluded that SR is hardly with dopant anion movement during redox transformations of polyaniline. The relaxation processes during the oxidation of poly(3,4-ethylenedioxythiophene) in propylene carbonate solution were studied by Noël et al. (2003). They stated that for a fixed value of waiting potential E_w, an increase

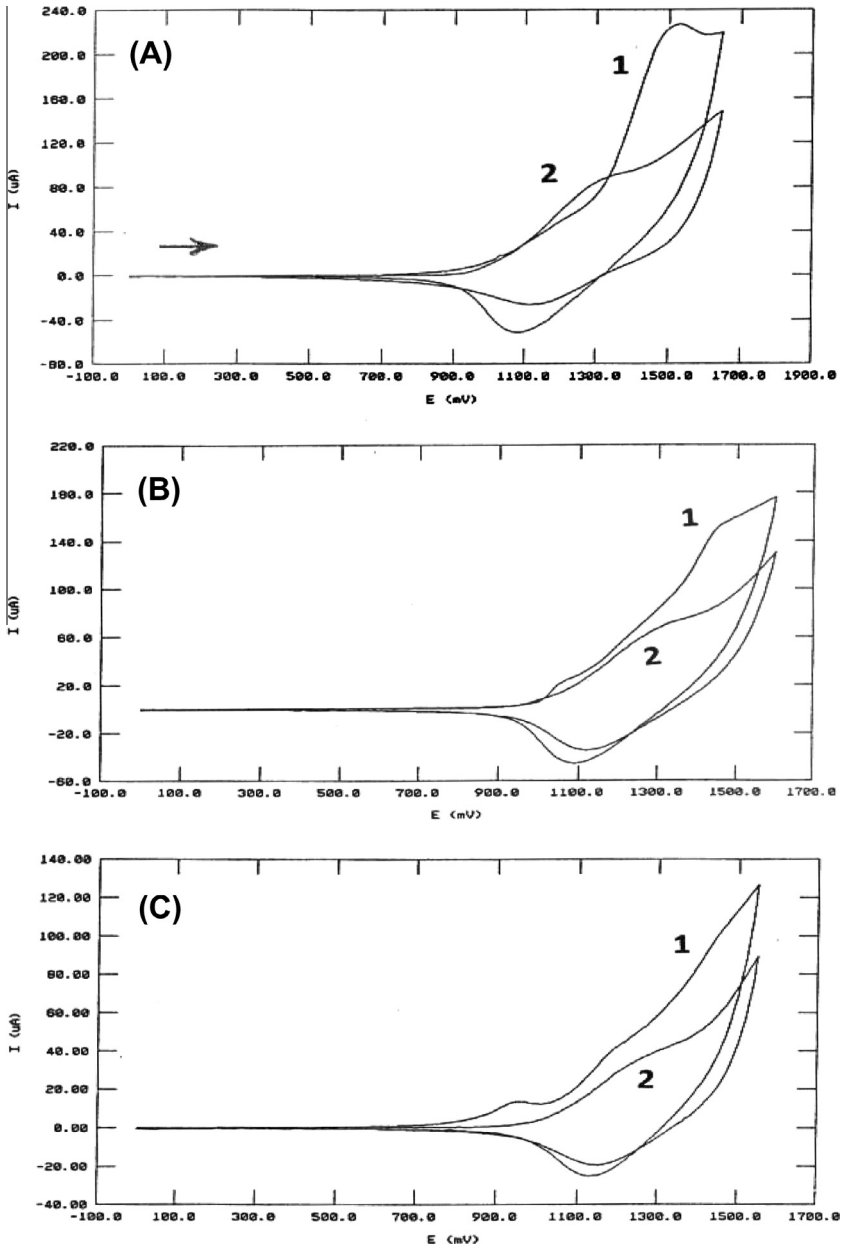

Figure 6 Cyclic voltammograms of PTA film on Pt-electrodein 0.05 $TBAPF_6$ + AN solution at scan rate 100 mV s^{-1}; (**1**) first wave after holding of electrode for t_w = 20 h at 0 V (**2**) steady state wave. The films were electrosynthesised: (A) chronoamperometrically in DCE. (B) Chronoamperometrically in DCM. (C) Potentiodynamically in DCM.

of the anodic peak current and the peak potential as a function of wait time t_w was observed. On the other hand, for a fixed value of t_w, a linear relationship between the anodic peak potential and E_w was found. In order to quantitate the electro-mechanical stress during the waiting time, an anodic over-tension in relation to the conformational relaxation. Otero and Abadıas (2007) presented a model of electrochemically stimulated conformational relaxation. According to this model (Otero and Abadias, 2007), the conformational relaxation model a description and quantitation of these results. They stated that time and current on the maxima keep memory of the compaction potential and the reduction time. They considered that it could quantitatively store conformational information (memory) in a continuous way by folding and packing chains of conducting polymers at increasing cathodic overpotentials, and it could then quantitatively read the stored information by oxidation.

In this work the effect of solvent on the relaxation process was investigated. The stable films were subjected to relaxation study in different solvents. Dry acetonitrile AN, 1, 2-dichloroethane DCE, 1, 1-dichloromethane (DCM), and nitrobenzene (NB) were used as solvents. $TBAPF_6$ was used as electrolyte in all used solvents. The PTA films were prepared and studied in the same solvent, the results showed that no significant change in the relaxation was recorded, as shown in Fig. 5. This behaviors were the same as 3-bromothiophene in previous work (El-Maghraby et al., 2010). The AN was considered as the best solvent to study the relaxation effect. So for films that prepared in

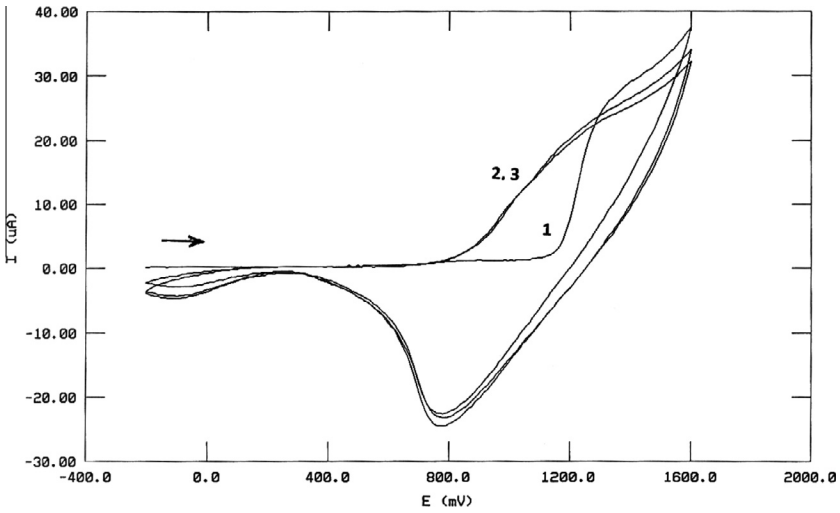

Figure 7 Successive cyclic voltammograms of 3-thiopheneacetonitrile film on Pt-electrode in NB + 0.05 $TBAPF_6$ solution at scan rate 100 mV s^{-1}; (**1**) relaxed wave after wait time 1 h**, 2, 3** steady state waves. Electrosynthetic media: 0.2 M thac + DCM + 0.02 $TBAPF_6$ at 5 C by galavanostatic method.

other solvents, they transferred into media of AN with supporting electrolyte for further relaxation studies. Fig. 6 shows cyclic voltammograms of 3-thiopheneacetonitrile film on Pt-electrode in 0.05 M $TBAPF_6$ + AN solution at scan rate 100 mV s^{-1}; (1) first wave after holding of electrode for t_w = 20 h at 0 V. (2) steady state wave. The films were electrosynthesised: (A) chronoamperometrically in DCE. (B) Chronoamperometrically in DCM. (C) Potentiodynamically in DCM. As shown from Fig. 6A, the anodic peak appears some what higher and shifted to positive potentials by 200 mV. The significant behavior in this case, the cathodic peak of the relaxed peak was observed shifted into more negative potentials by a few tens of mV and had more cathodic current than steady state peak. This behavior appeared only in the case of AN solvent while in other solvents no difference was noted as shown in Fig. 5. This behavior has been checked for films that prepared in all used solvents (with different techniques) and transferred into media of AN as shown in Fig. 6A and B.

Fig. 7 shows the results of PTA film on Pt-electrode in NB + 0.05 M $TBAPF_6$ solution at scan rate 100 mV s^{-1}. As shown from the profile PTA was subjected to relaxation, where first wave was shifted to more positive potential and the slope of the wave had a value different from that of the steady state wave. Fig. 7 shows the difference between the first cycle and several cycles. The effect of AN, DCM, and THF solvents on memory effect in poly(titanocene-propyl-pyrrole) was studied (Vorotyntsev et al., 2003). The effect was explained as due to either a greater ohmic potential drop inside the film, or a gradual increase of the resistance of the matrix.

The effect of electrolyte on relaxation was studied. The relaxation measurements were carried out using different supporting electrolytes. $TBAPF_6$, $TBAClO_4$, $TEAClO_4$, and $LiClO_4$ were used. By the same way as before (Abou-Elenien et al., 2004) it was found that, the most sharp peak was obtained using $TBAPF_6$, this is in agreement with the literature. Hexafluorophosphate anion gives the most sensitive film, which has the lowest relaxation time and the higher sharpness of the peak height which was clearly proved before (Abou-Elenien et al., 2004). Pern and Frank (1990) studied the effect of electrolyte on conducting polymers. It was found that the size of the dopant ion affects the oxidation kinetics and the electrical conductivity of the film. Recently, (Cerri et al., 2006 and Pigani et al., 2006) compared the effect of $LiClO_4$ and $TBAPF_6$ electrolyte on relaxation phenomena in polysubstituted thiophene and found that fast relaxation in the case of $TBAPF_6$ was due to an enhanced ionic mobility inside a non-compact polymer. In slow relaxation of the polyaniline, the amount of polymer to be oxidized in a following cycle depends upon the waiting time at the reduction potential. The memory effect was explained in terms of charge trapping (which lowers the peak magnitude) and in terms of conformational diffusion due to which the electroactivity units can oxidize more easily in short delays, this causes the shift to the left of the oxidation curve in the second scan (Borys et al., 2007). Due to the relative decrease of the stability of PTA films and the unclear peaks in media of AN, I could not determine the relaxation time as in the previous work (Abou-Elenien et al., 2004).

4. Conclusion

In this report, I studied the characterization of the TA and PTA. The polymer film was electrodeposited on Pt electrode surface with $TBAPF_6$ electrolyte. In electrosynthesis I used some electrochemical modes such as potentiodynamic, chronoamperometric, and galvanostatic techniques to obtain most stable films. Effect of solvents on electrodeposition has been studied. The solvents that have low donor number (DCE, DCM) were candidate to product PTA. The relaxation effect of the polymer was studied. The best solvent to study the relaxation was AN with $TBAPF_6$ electrolyte. An important point is on the cathodic part of the voltammograms, the reverse relaxed peak of the reduction side was appeared similar to relaxation. A negative shift of the first cathodic peak potential and an increase in cathodic current was observed. It was found that after *p*-doping and leaving the polymer film for a long wait time, they became nonconducting. This behavior indicates

to egress of the counter anion from the polymer film and a hard decrease in conductivity.

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